

7.—THE ESSENTIAL OILS OF THE WESTERN AUSTRALIAN EUCALYPTS.

PART III.

THE OILS OF *E. SALMONOPHLOIA*, F. v. M., and *E. TETRAGONA*, F. v. M.

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EUCALYPTUS SALMONOPHLOIA.

E. salmonophloia, the salmon gum, occurs over a large area of country roughly defined by the Midland and Southern railways from Mullewa to Gnowangerup, and extending as far eastwards as Kalgoorlie and Salmon Gums. It is described in the "Key to the Eucalypts of Western Australia" (Forests Department, Bulletin 34).

The material used in the present investigation was collected by Mr. G. H. Burvill, from Reserve 8102, about half a mile north of Circle Valley, near Salmon Gums. It was obtained about the middle of August, 1934, from vigorous sucker growth about 15 feet high, growing from old stumps, and was identified by the Government Botanist, Mr. C. A. Gardner. The leaves are copiously dotted with oil glands, and their venation is characteristic of the cineol-pinene oils which contain no phellandrene.

Baker and Smith (1920) have investigated the oil of the salmon gum obtained from material collected at the same time of the year (July or August), but from an unknown locality in Western Australia. A comparison of their results with those of the present investigation is therefore of interest.

	Baker and Smith.	Present Author.
Yield	1.44 per cent.	1.40 per cent.
Specific Gravity*	0.9039	0.9137
Refractive Index	1.4681	1.4731
Specific Rotation	+ 6.3°	- 4.12°
Solubility in 70 per cent. alcohol ...	In 3½ volumes	In 1¾ volumes
Saponification value	4.9	14.0
Cineol	48 per cent. (a)	46.4 per cent. (b)
Amount volatile below 183°	91 per cent.	76.5 per cent.
(a) By phosphoric acid.	(b) By <i>o</i> -cresol.	

The differences between the oils centre around the comparative absence of high boiling material in the oil distilled by Baker and Smith, and may be due either to a difference in origin of the two specimens, or to the possibility that the distillation by Baker and Smith was not carried to completion. The first supposition is not in agreement with the views of Baker and Smith on the constancy of composition of oils from a given species of *Eucalyptus*, whilst the second is not in accord with the observed yields. It must be borne in mind, however, that the material used by Baker and Smith would be in a much drier condition than that used in the present investigation, a higher percentage yield of oil therefore being obtainable without distillation to completion.

*Physical properties are given at 20°C unless otherwise stated.

Apart from this, the oils were very similar to one another. Both contained phenols and high boiling aldehydes, and their cineol contents were very similar. Phellandrene was not detected in either, whilst the amount of pinene present was appreciably lower than in otherwise somewhat similar oils; aromadendrene was identified in both.

The esters in the present oil are made up almost entirely of geranyl acetate, whilst about 85 per cent. of the alcohol content is geraniol. There are at least three distinct phenols present, one of which is, in all probability, the solid phenol australol, whilst the other two have not yet been obtained in crystalline form. One of these gives a purple colouration with ferric chloride, whereas the other gives a permanent deep green colour. They have not yet been obtained in sufficient quantity to be fully characterised or identified. On distillation, no separation of white insoluble material was noted as recorded in the oils previously described in this series (Watson, 1934-35), although a small amount of precipitate had settled out during the storage of the oil. Nearly 80 per cent. of the oil was volatile below 195° C. and this rectified oil contained about 54 per cent. of cineol, an amount considerably below the Pharmacopœial requirement for a medicinal eucalyptus oil.

Botanically and in the field, *E. salmonophloia* shows closest similarity to *E. Flocktoniae*, in the texture, character and colour of the bark, the colour of the heartwood, the habitat and in general appearance. The chemical nature of their oils, however, indicates that they are of rather different types. Thus the oil from the salmon gum does not form a precipitate on distillation, and contains phenols and high boiling aldehydes. The presence of the latter is considered by Baker and Smith to be indicative of a higher type of eucalypt.

EUCALYPTUS TETRAGONA.

E. tetragona, the mealy gum or blue mallee, occurs in the southern portion of Western Australia, from the Stirling Range eastwards to Cape Arid. Its leaves are thick and rigid and are covered with a white meal; they are only sparsely dotted with oil glands and the veins are divergent and spaced, the intramarginal vein being removed from the edge.

The material used was collected by Mr. Burvill in May, 1935, in the country adjacent to the south boundary of Esperance Location 444, about 1½ miles north-west of Scaddan, and was identified by Mr. Gardner.

The oil, which distilled very slowly, was pale green in colour, had a pleasant odour and was viscous and sticky. It consisted chiefly of high boiling substances, less than 25 per cent. being volatile below 230° C. This more volatile portion consisted of cineol, *d*-pinene and *l*-phellandrene, whilst the higher boiling material consisted mainly of aromadendrene and the serquiterpene alcohol, eudesmol, together with smaller amounts of geraniol, phenols, aldehydes and esters.

The presence of eudesmol in quantity in this oil is of interest, its occurrence in Western Australian oils having been recorded only once previously, in the oil of *E. accedens*. In the latter case, eudesmol was only present in small amount,* and was not accompanied by phellandrene.

*Baker and Smith, p. 123: "Eudesmol was detected."

EXPERIMENTAL.

EUCALYPTUS SALMONOPHLOIA.

The leaves were steam distilled in the form of the terminal branchlets and they were in a partly air-dried condition. The oil distilled very rapidly at first, about 80 per cent. coming over in the first hour, the distillation being complete in 3½ to 4 hours; the yield of undried oil was 1.40 per cent. by weight. The oil was pale yellow in colour and had a fairly pleasant odour. The dried oil, when examined some seven months later, was golden yellow in colour, and a small amount of insoluble material had separated out. In addition to those already given, the oil had the following properties:—Acid value, 2.2; saponification value (a) hot, 11.8, (b) cold, 11.1; acetyl value (a) hot, 61.7, (b) cold, 54.1.

The high solubility in alcohol indicates a low proportion of hydrocarbons.

The cold saponification value is a measure of the amount of geranyl acetate present (Baker and Smith, p. 367) and corresponds to 3.9 per cent. of this ester. The hot saponification value corresponds to 4.1 per cent. of esters calculated as $C_{12}H_{20}O_2$, leaving the small amount of 0.2 per cent. of esters other than geranyl acetate. The saponification value of the acetylated oil, determined in the cold, corresponds to 11.6 per cent. of geraniol, whilst that determined hot corresponds to 13.7 per cent. of alcohols calculated as $C_{10}H_{18}O$, a difference of 2.1 per cent. of alcohols other than geraniol. The oil slowly restored the colour to Schiff's reagent, showing the presence of aldehydes; estimation by means of hydroxylamine hydrochloride gave 4.5 per cent. by weight of aldehydes calculated as $C_{10}H_{14}O$. With alcoholic ferric chloride, a deepening in colour indicated the presence of phenols, estimated volumetrically to be 4.8 per cent. The oil gave the usual reactions for aromadendrene.

FRACTIONATION.

300 Grams of the oil were distilled under atmospheric pressure and the following fractions separated:—

Fraction.	Boiling Range.	Amount.	Specific Gravity.	Refractive Index.	Specific Rotation.
1	Up to 152°C.	1.7 per cent.	0.8666	1.4493	} + 11.05° + 4.98° — 3.98° — 12.46° — 26.05°
2	152–162°	1.5 „	0.8829	1.4577	
3	162–174°	50.45 „	0.8970	1.4653	
4	174–182°	22.8 „	0.9097	1.4674	
5	182–195°	2.5 „	0.9230	1.4733	
6	195–230°	10.15 „	0.9549	1.4871	

The residue (10.75 per cent.) was further fractionated at a pressure of 24 mms.

7	114–135°	2.8 per cent.	0.9550	1.4973	— 32.77°
8	135–160°	1.35 „	0.9670	1.5072	— 12.20°
9	160–190°	0.95 „	0.9861	1.5096	+ 4.10°

The distillation was then stopped owing to decomposition.

Fraction 1 was colourless and strongly acidic, containing an appreciable amount of acetic acid.

Fraction 2 was pale yellow in colour and had a pinene-like odour. From the combined fractions 1 and 2, an oil rich in pinene was separated and from which the nitrosochloride was isolated in quantity.

Fraction 3 was pale yellow in colour and had a pleasant cineol-like odour. Its cineol content was 52.2 per cent.; acid value, 1.85; saponification value, 5.4 (corresponding to 1.9 per cent. of geranyl acetate); acetyl value, by cold hydrolysis, 16.1 (corresponding to 2.9 per cent. of geraniol), and by hot hydrolysis, 18.9 (corresponding to 3.7 per cent. of alcohols calculated as $C_{10}H_{18}O$). It contained no phenols or aldehydes.

Fraction 4 was practically colourless and had a pleasant camphoraceous odour. Its cineol content was 62.8 per cent. and it contained no aldehydes or phenols. Its acid value was 1.4; saponification value, 12.7 (corresponding to 4.4 per cent. of geranyl acetate); acetyl value, by cold hydrolysis, 35.8 (corresponding to 12.5 per cent. of geraniol), and by hot hydrolysis, 42.5 (corresponding to 14.85 per cent. of alcohols calculated as $C_{10}H_{18}O$). Phellandrene was absent.

Fraction 5 was small and had a very pale yellow colour. Fractions 5 and 6 both contained appreciable amounts of cineol.

Fraction 6 was clear yellow in colour and had strong negative rotation, due partly to aldehydes, since the fraction restored the colour to Schiff's reagent. The acid value was 2.3; saponification value, 16.7 (corresponding to 5.8 per cent. of esters calculated as geranyl acetate); cold acetyl value, 150 (corresponding to a total amount of 52.3 per cent. of geranyl acetate or 36.5 per cent. of geraniol in the original fraction); hot acetyl value, 172 (corresponding to a total of 60.0 per cent. of geranyl acetate, or to 42.6 per cent. of alcohols, calculated as geraniol, in the original fraction).

Small quantities of two distinct phenols were present in this fraction. Extraction of the acidic substances gave an oil which partly crystallised; the crystals, when dissolved in alcohol, gave a transient green colour with ferric chloride, the solution then becoming yellow, whilst the liquid gave a fine purple colour when similarly treated. The crystalline body was probably australol (Baker and Smith, p. 396), whilst the phenol giving the purple colouration does not appear to have been described.

Fraction 7 was clear yellow in colour. With ferric chloride it gave a strong orange colouration (possibly due to the presence of another phenol), tinged with purple; high boiling aldehydes and aromadendrene were present.

Fraction 8, which was somewhat deeper in colour, gave a clear purple colouration with ferric chloride; it restored the colour to Schiff's reagent and gave the usual reactions for aromadendrene.

Extraction of the phenolic substance gave an oil of characteristic phenol-like odour. It could not be induced to crystallise; fusion with phthalic anhydride gave no characteristic colouration, whilst coupling with diazotised benzidine gave a deep orange red dye. Neither its benzoyl nor bromine derivatives could be obtained in crystalline form.

Fraction 9 was deep golden yellow in colour and was very viscous. It gave good reactions for aromadendrene, and with ferric chloride gave a permanent deep green colouration. It was not found possible to separate the phenol producing this colour in crystalline form, nor to prepare crystalline derivatives from it.

EUCALYPTUS TETRAGONA.

The oil was distilled from thoroughly air-dried leaves; it distilled extremely slowly, a yield of 0.48 per cent. being obtained on 14 hours' distillation. The dry oil had the following properties:—Specific gravity, 0.9390;

refractive index, 1.4954; specific rotation, $+ 3.65^\circ$; acid value, 1.0; saponification value (hot), 6.8, (cold), 6.6; acetyl value (hot), 107.5, (cold), 19.8; completely soluble in 1 volume of 80 per cent. alcohol, almost so in 10 volumes of 70 per cent. alcohol.

The hot saponification value corresponds to 2.4 per cent. of esters calculated as $C_{12}H_{20}O_2$, and the cold value to 2.3 per cent. of geranyl acetate. The cold acetyl value is equivalent to a geraniol content of 3.6 per cent., whilst the difference between the cold and hot values is equivalent to 32.0 per cent. of alcohols calculated as eudesmol, $C_{15}H_{26}O$. The cineol content (by *o*-cresol) was 15.4 per cent.; phenols (by caustic absorption), 3.7 per cent.; aldehydes (by hydroxylamine), 0.80 per cent. The aromadendrene content was so high that the colouration with bromine vapour completely obscured the qualitative test for cineol.

FRACTIONATION.

Sixty Grams of the oil were distilled and the following fractions separated:—

Fraction.	Boiling Range.	Amount.	Specific Gravity.	Refractive Index.	Specific Rotation.
1	Up to 160°C .	7.4 per cent.	0.8599	1.4697	$+ 20.2^\circ$
2	$160-195^\circ$	12.3 „	0.8603	1.4724	$+ 12.3^\circ$
3	$195-230^\circ$	5.2 „	0.8758	1.4836	$+ 9.3^\circ$

The residue (75.1 per cent.) was then further fractionated at a pressure of 23 mms.

4	$110-140^\circ$	4.0 per cent.	0.9245	1.4958	—
5	$140-160^\circ$	26.1 „	0.9526	1.5043	$+ 4.3^\circ$
6	$160-170^\circ$	35.6 „	—	1.5065	—
7	$170-180^\circ$	4.2 „	—	1.5080	—
	Residue	5.1 „			

Fraction 1 was colourless, had a pleasant terpene-like odour and consisted mainly of *d*-pinene.

Fraction 2 was colourless and consisted of cineol, *d*-pinene and *l*-phellandrene (nitrosite, m.p. and mixed m.p. with an authentic specimen from the oil of *E. dives*, 110°C).

Fraction 3 had a faint yellow colour, contained small amounts of cineol and *l*-phellandrene, and gave a reddish colour with ferric chloride.

Fraction 4 was clear yellow in colour; it had saponification value 30.8 and gave a purplish-red colour with ferric chloride; it contained no aldehydes but gave very strong reactions for aromadendrene.

The remaining fractions appeared to be free from phenols, but all contained considerable amounts of aromadendrene, particularly fraction 5. High boiling aldehydes were present, to greatest extent in fraction 6; esters were present to a lesser extent than in fraction 4, the saponification values of fractions 5 and 6 being 7.4 and 4.3 respectively.

Fraction 7 consisted very largely of eudesmol. It solidified almost immediately and after drying on a porous tile and recrystallising from dilute alcohol, gave the characteristic needle crystals of eudesmol (m.p. 79°). Frac-

tion 6 had a cold acetyl value 22.3, and a hot acetyl value 135.5, the difference corresponding to nearly 45 per cent. of alcohols calculated as eudesmol. On seeding, the eudesmol crystallised out rapidly.

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